

PATENT SPECIFICATION

NO DRAWINGS

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1,095,485

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COMPLETE SPECIFICATION

Improvements in or relating to Polyhydroxy-Urethanes

We, DYNAMIT NOBEL AKTIENGESELLSCHAFT, a German Company, of 521 Troisdorf, Near Cologne, Germany, do hereby declare the invention, for which we pray

that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to polyhydroxyurethanes and is concerned with a process for the production of shaped structures from cross-linked polyhydroxyurethanes.

It is known from for example United States Patent Specification No. 2,930,779 and No. 2,918,478 that water-soluble polyhydroxyurethanes can be obtained by reacting polyvinylene carbonates with amines. Aqueous solutions of these polyhydroxyurethanes can be processed by conventional methods into shaped structures such as fibres, films, coatings or the like. Such structures are, however, of little use for many industrial applications on account of their low mechanical strength. They have *inter alia* an unsatisfactory tensile strength and a low dimensional stability. An attempt also has been made to react polyhydroxyurethanes with formaldehyde, however, the products thus obtained can only be processed into shaped structures with very great difficulty and in the presence of modifying agents on account of their properties.

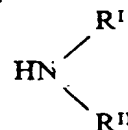
According to the present invention there is provided a process for the production of a shaped structure formed from a cross-linked polyhydroxyurethane, which comprises reacting a primary or secondary hydroxyalkylamine with a polyvinylene carbonate or with a vinylene carbonate copolymer having recurring units at least 50% of which are vinylene carbonate units to obtain a polyhydroxyurethane, forming the polyhydroxyurethane into a shaped

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structure, and thereafter cross-linking the shaped polyhydroxyurethane to obtain the desired structure.

Polyvinylencarbonates of various relative viscosities and also vinylencarbonate copolymers consisting predominantly of vinylencarbonate units (i.e. having recurring units at least 50% of which are vinylencarbonate units) can be used in the process of the present invention. Suitable copolymers are copolymers of vinylencarbonate with, for example, acrylonitrile, acrylamide, esters of acrylic acid or methacrylic acid, olefins, such as ethylene and propylene, butadiene, styrene or substituted styrenes such as dimethylstyrene, vinyl ethers, vinyl chloride, vinylidene chloride or vinyl esters, such as vinylacetate and vinylpropionate.

The hydroxyalkylamine may be a primary or secondary amine. Suitable amines for carrying out the process of the present invention are those which contain at least one hydroxyl group as well as the amino group, e.g. they may be hydroxyalkylamines of the general formula:



wherein R^I is hydrogen, or an aliphatic or cycloaliphatic alkyl or hydroxyalkyl group having from 1 to 6 carbon atoms and R^{II} is an aliphatic or cycloaliphatic hydroxyalkyl group having from 1 to 6 carbon atoms. Particularly preferred amines are, for example, ethanolamine, 4-hydroxycyclohexylamine, 4-aminobutanol, diethanolamine and N-methylisopropanolamine.

A single hydroxyalkylamine may be reacted with the vinylene carbonate polymer or copolymer in which case a homogeneous

polyhydroxyurethane is obtained. Alternatively, a mixed polyhydroxyurethane may be produced by reacting the vinylene carbonate polymer or copolymer with a mixture of two or more hydroxyalkyl amines or a mixture of one or more hydroxyalkyl amines and one or more alkylamines.

It is not absolutely necessary for all the carbonate groups contained in the vinylene carbonate polymer or copolymer to be reacted with amine and to be converted into hydroxyurethane units. By way of example, a polyhydroxyurethane obtained from polyvinylencarbonate and ethanolamine, in which only about 60% of the carbonate groups are reacted to form the hydroxyurethane grouping, can be processed to form shaped structures which can then be cross-linked.

In order to prepare the polyhydroxyurethane, polyvinylencarbonate or the copolymer consisting predominantly of vinylencarbonate units may be thoroughly mixed, with or without addition of a solvent, with the hydroxyalkylamine or with a mixture of amines comprising a hydroxyalkylamine. Without using solvents, the vinylencarbonate polymer or copolymer is usually readily dissolved at a temperature of from 10 to about 30°C. with the formation of a viscous solution of the corresponding polyhydroxyurethane in the amine(s). Preferably, the amount of amine present is in excess of from 10 to 20 times the theoretically necessary quantity. The viscous solution can then be introduced into for example methanol or acetone whereby the polyhydroxyurethane is precipitated as a colourless, fibrous mass. This mass is then washed with for example methanol or acetone until free of unreacted amine and is then dissolved in water. The aqueous solution thus obtained, which can be prepared in a more or less highly concentrated form as desired depending on the intended purpose of use, can then be processed by known methods, for example by casting or spinning, to form shaped structures such as films or coatings. However, these structures do not have the required strength or dimensional stability and are usually tacky. They can however be converted into structures having higher strength by cross-linking the polyhydroxyurethane from which they are made. The cross-linking can be effected by heat or by infra red radiation.

Cross-linking is preferably carried out at high temperature, it being possible for the temperature to vary within wide limits. However, it is advantageous to select a temperature between approximately 60 and approximately 100°C. because in this range the cross-linking reaction proceeds at a

suitable speed and leads to shaped structures of high strength. The period of time necessary to effect cross-linking depends on the temperature at which the cross-linking is carried out. For example, if a polyhydroxyurethane film produced from polyvinylencarbonate and ethanolamine and which, in the untreated state, has a tensile strength of 6.1 kg/cm² with an elongation at break of 380%, is heated for 215 hours at 60°C., the tensile strength is increased to 330 kg/cm² and the elongation at break is reduced to 80%. The same tensile strength and elongation at break values are obtained after 70 hours with a cross-linking temperature of 80°C. and after 50 hours at a cross-linking temperature of 100°C. A maximum strength of 952 kg/cm² was acquired by this film after 90 hours at 80°C. and after 80 hours at 100°C.

Heating for a longer period leads to an increasing embrittlement of the film. Further, raising of the reaction temperature to above 100°C. generally does not provide any higher strength for the film but leads to embrittlement, although it is possible thereby to obtain relatively quickly a film of medium tensile strength (400 to 500 kg/cm²).

Depending upon the intended purpose of use, it is possible to produce structures of different strength and elasticity and also with different behaviour with respect to water and chemical agents by suitable cross-linking temperature control, by varying the time for which cross-linking is effected and by suitable choice of the amine used to produce the polyhydroxyurethane.

Cross-linked polyhydroxyurethanes are especially suitable for the production of non-tearing and elastic films and coatings, and also for the finishing of textiles.

The following Examples illustrate the invention:

EXAMPLE 1

At a temperature of from about 10 to about 30°C., a large excess of freshly distilled ethanolamine (about 500 g.) was added to 30 g. of polyvinylencarbonate having a relative viscosity of 2.1 and thoroughly admixed therewith. After a short time, the polyvinylencarbonate had reacted and a colourless viscous solution of polyhydroxyurethane had formed. This was introduced with stirring into acetone whereby the polyhydroxyurethane precipitated as a colourless, fibrous mass. This was washed with acetone until free from amine and was then dissolved in cold water. If desired, the acetone can be replaced by methanol or other suitable precipitation agent. The polyhydroxyurethane had good solubility in water and it was thus easily possible to prepare aqueous solutions of varying high concentration depending on

the intended purpose of use. By working up the precipitation bath and the washing liquid, the excess amine was easily recovered.

5 For the manufacture of films, an approximately 10 to 20% aqueous solution of the polyhydroxyurethane was prepared and this was poured on to siliconised glass plates or on to polyethylene plates. After about 12
10 hours, a film of polyhydroxyurethane could be lifted from the plate. The tensile strength and the elongation at break of this foil were then determined, the results being as follows:

15 Tensile strength: 6.1 kg/cm²
Elongation at break: 380%

The film was thereafter cut into three pieces A, B and C of the same size, and each piece was cross-linked at a different
20 temperature.

Piece A after being cross-linked at 60°C. for 215 hours had the following mechanical properties:

25 Tensile strength: 330 kg/cm²
Elongation at break: 80%

Piece B after being cross-linked at 80°C. for 90 hours had the following mechanical properties:

30 Tensile strength: 952 kg/cm²
Elongation at break: 20%

Piece B was thereafter stored for 15 hours in an atmosphere of 65% relative humidity and was then found to have the following mechanical properties:

35 Tensile strength: 796 kg/cm²
Elongation at break: 50%

Piece C after being cross-linked at 100°C. for 80 hours had the following mechanical properties:

40 Tensile strength: 940 kg/cm²
Elongation at break: about 20%

Piece C was then stored for a further 15 hours in an atmosphere of 65% relative humidity and was then found to have the
45 following mechanical properties:

Tensile strength: 743 kg/cm²
Elongation at break: 55%

EXAMPLE 2

50 A polyhydroxyurethane film was produced from a polyvinylencarbonate having a relative viscosity of 1.70 and diethanolamine by the procedure described in Example 1. Before cross-linking, the film had the following mechanical properties:

55 Tensile strength: 150 kg/cm²
Elongation at break: 50%

After cross-linking for 48 hours at 60°C., the mechanical properties were as follows:

60 Tensile strength: 400 kg/cm²

Elongation at break: 25%
After a further 15 hours storage in an atmosphere of 65% relative humidity, the cross-linked film had the following mechanical properties:

65 Tensile strength: 309 kg/cm²

Elongation at break: 40%

EXAMPLE 3

A polyhydroxyurethane film was produced from a copolymer of vinylencarbonate and vinylacetate containing 90%
70 by number of vinylencarbonate units and ethanolamine by the procedure described in Example 1. In the uncross-linked state, the film had the following mechanical properties:

Tensile strength: 4.6 kg/cm²

Elongation at break: 305%

After 90 hours storage at 80°C., mechanical properties of the film were:

Tensile strength: 727 kg/cm²

Elongation at break: 20%

After a further 15 hours storage in an atmosphere of 65% relative humidity, the mechanical properties of the cross-linked film were as follows:

Tensile strength: 536 kg/cm²

Elongation at break: 45%

EXAMPLE 4

A polyhydroxyurethane film was produced from polyvinylencarbonate having a relative viscosity 1.93 and a mixture of 80 parts
90 by weight of ethanolamine and 20 parts by weight of diethanolamine using the procedure described in Example 1. The non-cross-linked film had the following mechanical properties:

Tensile strength: 20 kg/cm²

Elongation at break: 250%

After being cross-linked for 90 hours at 80°C, the mechanical properties of the film
100 were as follows:—

Tensile strength: 705 kg/cm²

Elongation at break: 15%

After a further storage for 15 hours in an atmosphere of 65% relative humidity, the
105 mechanical properties of the cross-linked film were as follows:

Tensile strength: 543 kg/cm²

Elongation at break: 30%

WHAT WE CLAIM IS:—

1. Process for the production of a shaped structure formed from a cross-linked polyhydroxyurethane, which comprises reacting a primary or secondary hydroxyalkylamine with a polyvinylene carbonate or with a
115 vinylene carbonate copolymer having recurring units at least 50% of which are vinylene carbonate units to obtain a polyhydroxyurethane, forming the polyhydroxyurethane into a shaped structure, and thereafter cross-linking the shaped polyhydroxyurethane to obtain the desired structure.

2. Process according to Claim 1, wherein the cross-linking is effected by heating the shaped polyhydroxyurethane to a
125 temperature of from 60 to 100°C.

3. Process according to Claim 1 or 2, wherein the cross-linking is effected by irradiating the shaped structure with infrared radiation.

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4. Process according to any one of Claims 1 to 3, wherein the polyvinylene carbonate or the vinylene carbonate copolymer is reacted with a mixture of primary or secondary hydroxyalkylamines.
5. Process according to any one of Claims 1 to 4, wherein the polyvinylene carbonate or the vinylene carbonate copolymer is reacted with a mixture of one or more primary or secondary hydroxyalkylamines and one or more alkylamines.
6. Process according to any preceding claim, wherein the hydroxyalkylamine is ethanolamine or diethanolamine.
7. Process according to any one of Claims 1 to 5, wherein the hydroxyalkylamine is 4-hydroxycyclohexylamine, 4-aminobutanol or N-methyl-isopropanolamine.
8. Process according to any preceding claim, wherein the vinylene carbonate copolymer is a copolymer of vinylene carbonate and a vinyl ester.
9. Process according to Claim 8, wherein the vinyl ester is vinyl acetate.
10. Process according to Claim 8, wherein the vinyl ester is vinyl propionate.
11. Process according to any one of Claims 1 to 7, wherein the vinylene carbonate copolymer is a copolymer of vinylene carbonate and acrylonitrile or acrylamide.
12. Process according to any one of Claims 1 to 7, wherein the vinylene carbonate copolymer is a copolymer of vinylene carbonate and an acrylic or methacrylic acid ester.
13. Process according to any one of Claims 1 to 7, wherein the vinylene carbonate copolymer is a copolymer of vinylene carbonate and an olefin.
14. Process according to Claim 13, wherein the olefin is ethylene or propylene.
15. Process according to any one of Claims 1 to 7, wherein the vinylene carbonate copolymer is a copolymer of vinylene carbonate and butadiene.
16. Process according to any one of Claims 1 to 7, wherein the vinylene carbonate copolymer is a copolymer of vinylene carbonate and styrene or a substituted styrene.
17. Process according to Claim 16, wherein the substituted styrene is dimethyl styrene.
18. Process according to any one of Claims 1 to 7, wherein the vinylene carbonate copolymer is a copolymer of vinylene carbonate and a vinyl ether.
19. Process according to any one of Claims 1 to 7, wherein the vinylene carbonate copolymer is a copolymer of vinylene carbonate and vinyl chloride or vinylidene chloride.
20. Process in accordance with Claim 1, for the production of a shaped structure formed from a cross-linked polyhydroxyurethane, substantially as described in any one of the foregoing Examples.
21. A shaped structure formed from a cross-linked polyhydroxyurethane, whenever produced by the process claimed in any preceding claim.
22. A shaped structure as claimed in Claim 21, in the form of a film or fibre.
23. A shaped structure as claimed in Claim 21, in the form of a coating.

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